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"SLIP EFFECTS" IN CONCENTRATED EMULSIONS

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"SLIP EFFECTS" IN CONCENTRATED EMULSIONS

by

R. Pal*, E. Rhodes** and N.A. Mansour***

ABSTRACT

In this study, rheological data obtained for various concentrated oil-in-water and water-in-oil emulsions from viscometers of different design and geometry have been analyzed and compared. The three types of viscometers used were the; FAN viscometer (coaxial cylinder type); Weissenberg Rheogoniometer (cone-and-plate) Brookfield viscometer (rotating bob in an infinite fluid).

In the case of oil-in-water emulsions, the flow curves obtained with the cone-and-plate viscometer are in close agreement with those given by coaxial cylinder viscometer only when the oil concentrations are below 70%. For concentrations greater than 70%, the flow curves obtained from the two instruments are appreciably different.

In the case of water-in-oil emulsions the flow curves obtained from different instruments are in agreement only when water phase concentrations are below 60%. For water concentrations greater than 60%, the flow curves obtained are significantly different.

The variation in the flow curves for the same concentration emulsions has been attributed to the presence of "slip-effects" in the cone-and-plate viscometer.

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"EFFETS DE GLISSEMENT" DANS LES ÉMULSIONS CONCENTRÉES

par

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RÉSUMÉ

Dans cette étude, on a analysé et comparé les données rhéologiques obtenues à propos de diverses émulsions concentrées d'huile dans l'eau et d'eau dans l'huile, au moyen de viscosimètres de conception et de géométrie différentes. Les trois types de viscosimètres utilisés étaient : le viscosimètre FAN (type cylindrique coaxial); le rhéogoniomètre de Weissenberg (cône et plaque) et le viscosimètre de Brookfield (bobine rotative dans un fluide infini).

Dans le cas des émulsions d'huile dans l'eau, les courbes de débit obtenues avec le viscosimètre à cône et plaque ne concordent étroitement avec celles données par le viscosimètre cylindrique coaxial, que si les concentrations d'huile se situent au-dessous de 70 %. Dans le cas de concentrations supérieures à 70 %, les courbes de débit obtenues avec les deux instruments diffèrent dans une mesure appréciable.

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Dans le cas des émulsions d'eau dans l'huile, les courbes de débit obtenues au moyen d'instruments divers ne concordent entre elles que lorsque les concentrations de la phase aqueuse se situent au-dessous de 60 %. Dans le cas de concentrations en eau supérieure à 60 %, les courbes de débit obtenues diffèrent nettement les unes des autres.

On a attribué la variation des courbes de débits obtenues avec des émulsions de même concentration à la présence d'"effets de glissement" dans le viscosimètre à cône et plaque.

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INTRODUCTION

A considerable amount of the world's crude oil is produced in the form of stable emulsions (1). Water-in-oil types of emulsions are mainly encountered in primary production. On the other hand, oil-in-water emulsions (also known as reverse emulsions) are more frequently encountered in secondary and tertiary oil recovery projects. Many situations exist where oil-in-water emulsions are deliberately made in order to reduce the high viscosity (and hence pumping cost) of crude oils (2-7). The use of emulsions to enhance oil recovery is receiving special attention in current years (8).

To evaluate the rheological properties of emulsions, instruments of many designs are available commercially. They fall into four main categories, viz: rotating bob in an infinite fluid, coaxial cylinder, cone-and-plate and capillary.

To ensure that the rheological properties determined are the properties of the emulsion and not artifacts produced by the method of investigation, it is very important and often necessary to obtain comparative data from viscometers of different designs. If different viscometers do not give the same rheological measurements, then it may be unwise to test the emulsions in simple viscometers and use the results to predict the behaviour of the same emulsion in pipelines, mixing equipment, etc. The main objective of this study was to analyze and compare emulsion rheological data obtained from viscometers of different designs and determine if "slip effects" were present. The emulsions used in the study were made up to represent emulsions which might be encountered in the heavy oil recovery industry.

EXPERIMENTAL

EMULSION PREPARATION:

Oil-in-water emulsions were prepared by the agent-in-water method at room temperature (-24°C). The oil phase was 73.3% by volume (white mineral oil) dissolved in 26.7% by volume carbon tetrachloride which was added to the mineral oil in order to make the density of oil phase equal to that of water

phase. In this way the creaming effect in the emulsions was eliminated. One percent by volume (based on the water phase) of non-ionic emulsifier Triton X-100, was added to deionized water and this mixture was slowly stirred until the emulsifier was completely dissolved. To this mixture of water and emulsifier, the required amount of the oil phase was slowly added and the mixture was sheared in a high shear machine (Gifford-Wood Model 1-LV Homogeneizer-Mixer) for about 15 minutes. To obtain more highly concentrated emulsions, more oil phase was added to the existing lower concentration emulsion and the mixture sheared again for 15 minutes. In the 76% emulsion, some air entrapment was noted and therefore the next higher concentration emulsions were made fresh.

Water-in-oil emulsions were prepared by the agent-in-oil method at room temperature (-25°C). The oil phase was the same as that used in the preparation of oil-in-water emulsions. 1.5% by volume (based on oil phase) of SPAN 80 (non-ionic emulsifier) was added to the oil phase and this mixture was stirred gently until the emulsifier dissolved completely. To this mixture, the required amount of deionized water was slowly added and the mixture was sheared in the Homo-mixer for about 15 minutes. To obtain higher concentration emulsions, more water was added and the mixture sheared again for 15 minutes.

VISCOMETERS USED:

a) Rotating spindle in an infinite fluid:

The Brookfield Synchro-lectric viscometer falls under this category. The Brookfield model used in this study was provided with 4 spindles (one cylindrical and 3 disc type) and had 8 speeds (60 rpm to 0.3 rpm). It is one of the simplest types of instrument and is widely used throughout many industries. A synchronous motor drives a cylinder or disc element which is immersed in a fluid at a constant speed of rotation. The force required to overcome the resistance offered by the

sample to this motion is derived from a beryllium copper spring which drives the immersed element. A dial at the top of the viscometer records the extent to which the spring is wound in overcoming the viscous resistance. Consequently the dial reading is proportional to the viscosity of the sample. The instrument can be calibrated with a known viscosity standard. For Newtonian fluids, this type of instrument is good for absolute measurements. For non-Newtonian fluids, this instrument is not so good for quantitative analysis. The viscosity of non-Newtonians will depend on the rate of shear at which they are measured and the geometry of the spindle makes it extremely difficult to calculate the shear rate. However, this instrument is still very useful for qualitative analysis. The shearing rate for a particular spindle (and a particular fluid) is proportional to the speed of rotation and the shear stress is proportional to the dial reading. Therefore, flow curves can simply be obtained by plotting dial readings against rpm.

For low viscosity Newtonian emulsions, a Brookfield adapter was used. The adapter consists of a precision cylindrical spindle rotating inside an accurately machined tube. Before collection of any experimental data, the adapter was calibrated with 8.7 cP (25°C) viscosity standard and the calibration constant was found to be the same as specified by the manufacturing Company.

b) Coaxial Cylinder Viscometer

The FAN viscometer (coaxial type) model 35 having a gap width of 1.17 mm was used in this study. The outer cylinder (R-1 rotor) had a radius of 1.8415 cm. The inner cylinder (B-1 bob) had a radius of 1.7245 cm. The Bob height was 3.8 cm. Six test speeds of 3, 6, 100, 200, 300 and 600 rpm were available. The test fluid was contained in the annular space or shear gap between coaxial cylinders and the outer cylinder was rotated. The torque on the inner cylinder was measured and the torque as a function of angular velocity provided the relation between shear stress and shear rate.

In this type of viscometer, the variation of the rate of shear throughout the sample depends on the width of the annular gap between the two cylinders. If this width is kept small, the variation in shear rate can be made insignificant and the shear rate can be assumed constant throughout the sample. For relatively large gaps, the mean rate of shear and the mean shear stress per unit length of cylinder are calculated at the geometric mean radius ($\sqrt{R_1 R_2}$). These are given by:

$$\dot{\gamma} = 2R_1 R_2 \Omega / (R_2^2 - R_1^2) = K_2 \Omega \quad (1)$$

and

$$\tau = \frac{T}{2 \pi R_1 R_2} = K_3 \text{ (D.R.)} \quad (2)$$

where D.R. is the dial reading.

However, if R_1 and R_2 are not close the above equations do not hold. Krieger and Maron (9) have shown that the rate of shear at the surface of the inner cylinder is given by an infinite series which converges rapidly when the ratio of R_2/R_1 becomes less than 1.2. For values of R_2/R_1 less than 1.2 the expression for the shear rate at the inner cylinder reduces to

$$\dot{\gamma} = \frac{4 \pi \Omega \beta^2}{\beta^2 - 1} \left[1 + k_1 \left(\frac{1}{\beta} - 1 \right) + k_2 \left(\frac{1}{\beta} - 1 \right)^2 \right] \quad (3)$$

where β , k_1 and k_2 are instrument constants given by

$$\beta = R_2 / R_1 \quad (4)$$

$$k_1 = \frac{\beta^2 - 1}{2 \beta^2} \left[1 - \frac{2}{3} \ln \beta \right] \quad (5)$$

$$k_2 = \frac{\beta^2 - 1}{6 \beta^2} \ln \beta \quad (6)$$

and in any experiment "s" is the slope of the logarithmic plot of dial reading against rotational speed, Ω , at a particular value of Ω used in the experiment.

Hence shear stress and the corresponding rate of shear can be found from Eqns. (2) and (3) respectively and the flow curve then follows directly by repeating the experiment over a range of speeds.

The calibration of the instrument was done with a 100 cP viscosity standard. Since R_2/R_1 was less than 1.2, Eqn. 3 was used to calculate the shear rate. Shear stress was determined by multiplying the known viscosity with the shear rate. From the known shear stress, K_1 was determined by using Eqn. 2. K_1 was found to be constant and was $0.5107 \text{ NM}^{-2}/\text{dial reading}$.

c) Cone-and-plate viscometer

The Weissenberg Rheogoniometer falls under this category. The R18 model was used in this study. The platen diameter was 100 mm and cone angle was 4° , giving a clearance between the cone flat (truncated tip) and adjacent plate of $171 \mu\text{m}$. The flat bottom platen of the Rheogoniometer was replaced by a platen with disked end to facilitate the use of emulsions in the instrument. This helped to retain the test material in the cone and plate assembly and data at higher shear rates could be obtained without any loss of material which could otherwise have occurred. The disked platen was calibrated with standards of known viscosities and edge effects were determined.

In this type of instrument, the cone remains stationary and the bottom platen is made to rotate. Since the angle between the cone and the flat platen is very small (and therefore the average gap width is corresponding small) the whole sample will be subjected to a constant rate of shear.

The linear velocity at radius r is Ωr and the gap width at radius r is $r \tan \alpha$. Hence, the rate of shear at radius r is given by

$$\dot{\gamma} = \frac{\Omega r}{r \tan \alpha} = \frac{\Omega}{\tan \alpha} \quad (7)$$

This means that the rate of shear is constant throughout the sample and is independent of r .

Further

$$\gamma(r) = \Omega / \alpha \quad (8)$$

since α is small.

Also since $\gamma = f(\tau)$ and γ is constant, then τ is constant.

Therefore

$$T = 2 \pi \tau \int_0^R r^2 dr \quad (9)$$

hence

$$\tau = \frac{3T}{2\pi R^3} \quad (10)$$

where T is the total torque on the top platen (cone). The flow curve can thus be constructed by plotting the rate of shear (Ω / α) against the corresponding shear stress ($3T/2\pi R^3$).

Brookfield viscosity standards of 100 cP and 1000 cP were used to calibrate this instrument. For different speeds of rotation, shear

rates were calculated according to Eqn. 8. Since shear rates and viscosity were also known, shear stresses were easily determined from

$$\tau = \mu \dot{\gamma} \quad (11)$$

The instrument calibration constant, K_T , was then determined from

$$\tau = K_T \Delta T t \dot{\gamma} \quad (12)$$

or

$$K_T = \frac{\tau}{\Delta T t \dot{\gamma}} \quad (13)$$

where ΔT is the transducer reading in microns and $t = 2\pi/\Omega$, in units of sec. rev.

The calibration constant, K_T , remained constant for both viscosity standards and its value was 6.72×10^{-4} NM²/microns(sec/rev)sec⁻¹.

PHOTOMICROGRAPHS

Photomicrographs of 70% oil-in-water emulsion were taken before and after shearing in the Weissenberg Rheogoniometer to see if the structure of the emulsion was altered during testing. The emulsion was sheared at a shear rate of 340.56 sec⁻¹ for 5 minutes.

A Zeiss optical microscope (with a camera attached) was used to take the photomicrographs. Emulsions were first diluted to about 20 times by glycerol and diluted sample was then placed on a dimple slide. Transmitted light with a green filter was used while taking photomicrographs.

RESULTS AND DISCUSSION

OIL-IN-WATER EMULSIONS RESULTS

Figures 1-3 show the flow curves of oil-in-water emulsions obtained for various oil concentrations with different instruments. Since it was not possible to calculate shear rates directly for the Brookfield viscometer, the data have been plotted as rpm versus the dial reading. The shape of the flow curves (characteristic of pseudoplastic/yield pseudoplastic fluids) obtained with different instruments are similar. However, an interesting point to note is that the Brookfield viscometer shows a definite yield stress for concentrated emulsions ($\phi \geq 76\%$) whereas the Weissenberg Rheogoniometer does not show any yield stress. The Fan viscometer also appears to show a yield stress for concentrated emulsions.

In Figure 4, the data of shear stress (τ) versus the shear rate ($\dot{\gamma}$) has been plotted on a log-log scale. The dotted line for the 30% emulsion indicates a viscosity measurement from the Brookfield adapter. The other lines shown on the figure are drawn through the Weissenberg Rheogoniometer data. Up to 60% concentration, there is good agreement between the instruments. For 70% emulsion, there is satisfactory agreement between the Fan viscometer and Weissenberg Rheogoniometer, although there is some scattering of data at the lower shear rates. This scattering could be due to reasons other than slip effects. For oil concentrations greater than 70% (i.e. for 76%, 80% and 82% emulsions), significant deviation is seen between the Weissenberg Rheogoniometer and the Fan viscometer data. The Rheogoniometer gives lower viscosities than the Fan viscometer at the same shear rate for the same emulsion. In Figure 5, the shear rate versus shear stress data has been replotted on a semi-log plot for oil concentrations greater than 70%. A nearly parallel shift in flow curves obtained from the Fan viscometer and the Rheogoniometer is obvious. For the 70% emulsion, a similar flow curve is obtained.

WATER-IN-OIL EMULSION RESULTS

Figures 6-8 show the flow curves of water-in-oil emulsions obtained for various water concentrations with different instruments. The Brookfield and Fan viscometers exhibit yield stress for concentrated emulsions ($\phi > 60\%$) whereas the Weissenberg Rheogoniometer does not show any yield stress.

Figure 9 shows the rheograms (τ vs. $\dot{\gamma}$) obtained with different instruments on log-log scale. The dotted lines for 0%, 10% and 20% emulsions indicate viscosity measurements from the Brookfield adapter. The other lines shown on the figure are drawn through the Weissenberg Rheogoniometer data. Up to 60% concentration, there is excellent agreement between the instruments. However, for water concentrations greater than 60%, flow curves obtained by different instruments are appreciably different for the same concentration emulsions. As in the oil-in-water emulsions, the Rheogoniometer gives lower viscosities than Fan viscometer at the same shear rate. Figure 10 shows that there is a nearly parallel shift in the flow curves obtained from the two instruments. For 60% emulsion, a single flow curve is obtained.

DISCUSSION

The shift in the flow curves obtained from the different instruments for the same emulsions can be explained by slip effects in the Weissenberg Rheogoniometer. Slip effects are known to exist in capillary tubes and small diameter pipes (10-15).

When a dispersed system enters a narrow capillary or tube, the dispersed phase shows a tendency to migrate away from the tube wall towards the tube axis. If this occurs there is a concentration fluctuation across the capillary with the major reduction in concentration in the layers adjacent to the capillary wall.

This phenomenon has actually been observed with a suspension of paper pulp (16). The fluid in the region close to the wall has a lower viscosity and this gives rise to an effective velocity of slip at the wall. Different diameter capillaries will then give different flow curves. Oldroyd has done a detailed analysis of slip effects in pipes (17).

It is highly likely that slip effects would also exist in cone-and-plate type viscometers. Due to preferred orientation of oil particles, a region adjacent to the cone and plate may form which is deficient in dispersed material. This will lead to a slip effect at the cone

and plate surface resulting in lower viscosity measurements. Boardman and Whitmore have also observed similar effects for flocculated china clay suspensions (18). These suspensions are normally Bingham plastic in nature. However, when these suspensions are studied in a cone and plate viscometer, they appear to behave as pseudo plastic fluids (with no yield stress) and the linear portion of the flow curve (shear stress vs. shear rate) is well below the true flow curve. The authors have attributed this abnormal behaviour to the presence of effective slip at the cone and platen surface.

It is highly likely that concentrated oil-in-water ($\phi \geq 76\%$) and water-in-oil ($\phi > 60\%$) emulsions exhibit some real yield stress (as shown by the Fan and Brookfield viscometers). Due to abnormal wall effects at the boundaries, they do not show this yield stress when the data are obtained from a cone-and-plate type viscometer.

ESTIMATION OF CONTINUOUS PHASE FILM THICKNESS

One can estimate the thickness of a continuous phase film formed adjacent to a cone and plate by theoretical analysis. figure 11 shows a schematic of the cone-and-plate viscometer. The cone tip is truncated in order to avoid disturbance of torque readings, although for the sake of accuracy, the point of the cone should touch the centre of the flat plate. Truncation of the cone tip would give only negligible error since the torque produced at the centre of the specimen is immeasurably small. The gap width (between truncated tip and flat plate) is so adjusted that the imaginary tip of the cone would touch the centre of the plate.

If "slip effects" are absent, then:

$$\text{shear stress } \tau = \frac{3}{2 \pi R^3} T \quad (14)$$

and shear rate is given by Eqn. (8).

where T is torque, Ω is angular velocity and α is cone angle. Therefore, by measuring the torque on the cone over a range of angular velocities Ω the flow curve of the fluid is obtained. For yield pseudoplastic fluid,

$$\tau = \tau_0 + K \gamma^n \quad (15)$$

where τ_0 is yield stress of the fluid and k and n are constants.

If "slip effects" are present, inhomogeneity development in the fluid adjacent to the walls, produces a layer of continuous phase film which possesses different flow properties from the bulk fluid. τ and γ (as given by Eqns. 9 & 8) are then only apparent values. In our analysis, we will make the following assumptions regarding the nature of the film fluid. Boardman and Whitmore (18) and Reiner (19) made similar assumptions when calculating wall effects in the case of Bingham plastic fluids.

- (i) It is Newtonian in nature.
- (ii) Its thickness is constant and is independent of the thickness of the bulk fluid.
- (iii) Its thickness is independent of the rate of shear.
- (iv) The liquid abstracted from the bulk fluid to form the wall layer is sufficiently small to produce a negligible change in the properties of the bulk fluid.

Now let the sheared volume of a cone-and-plate viscometer be completely filled with a yield pseudoplastic fluid except at the walls where it is bounded by a layer of liquid of thickness d and viscosity μ_w .

Then consider a narrow annulus of fluid situated at radius r . Because the annulus is narrow, αr , can be regarded as constant within it so that conditions in the annulus are equivalent to those between two parallel plates situated distance αr apart. The shear stress-shear rate relationship of a yield pseudoplastic fluid in such an annulus can very easily be shown to be

$$\tau = \tau_0 + K \left[\frac{\Omega r_2 - \frac{2 \tau d}{\mu_w}}{\alpha r - 2d} \right]^n \quad (16)$$

Thus τ changes with r and in general there yield two regions:

- (i) when $\tau < \tau_0$, the yield pseudoplastic fluid is unsheared, all relative motion occurring in the wall layers. This will be termed "lubricated plug flow". (Boardman and Whitmore (1963).
- (ii) when $\tau > \tau_0$, the yield pseudoplastic fluid and the wall layers are all fully sheared. This will be termed "complete laminar flow".

If the radius of transition from lubricated plug flow to complete laminar flow = ℓ_2 , Eqn. 15 gives

$$\tau_0 = \tau_0 + K \left[\frac{\Omega \ell_2 - \frac{2 \tau_0 d}{\mu_w}}{2 \ell_2 - 2d} \right]^n$$

or

$$\ell_2 = \frac{2 \tau_0 d}{\Omega \mu_w} \quad (17)$$

if $\ell_2 > R$ complete laminar flow is absent from the viscometer. From Eqn. 16 the condition is given by

$$\Omega = \frac{2 \tau_0 d}{\mu_w R}$$

or

$$\gamma_1 = \frac{2 \tau_0 d}{\alpha \mu_w R} \quad (18)$$

where γ_1 is the maximum apparent rate of shear without any complete laminar flow. Therefore, only lubricated plug flow exists for shear rates:

$$0 < \gamma < \gamma_1 .$$

For lubricated plug flow

It can be easily shown that

$$\tau = \frac{(\mu_w^2)(\gamma)}{2d} r \quad (19)$$

$$T = \int_0^R 2\pi r^2 \tau dr \quad (20)$$

or

$$T = 2\pi \frac{(\mu_w^2)}{2d} \gamma \frac{(R^4)}{4} \quad (21)$$

$$\tau = \frac{3}{2\pi R^3} [2\pi \frac{(\mu_w^2)}{2d} \gamma \frac{(R^4)}{4}]$$

or

$$\tau = \frac{(3 \mu_w^2 R)}{8d} \gamma \quad (22)$$

Thus the apparent flow curve (determined from cone-and-plate viscometer) of τ against r is linear. From the slope of this curve, one can determine d , the thickness of the film. Table I summarizes the values of film thickness obtained for various concentrated emulsions. It appears from the calculations (given in Table I) that the film thickness decreases as the concentration of dispersed phase in the emulsions is increased.

Table 1. Continuous phase film thickness

Type of Emulsion	dispersed phase concentration	slope of initial portion of τ vs γ curve	yield stress NM^{-2}	film thickness, μm
water-in-oil	70%	21	5	0.126
water-in-oil	75%	22.44	18	0.118
oil-in-water	76%	6.0	4	0.226
oil-in-water	80%	7.75	7	0.176
oil-in-water	82%	27.5	10	0.05

Variation of Viscosity with the Dispersed Phase Concentration

The viscosity of an emulsion depends upon several factors, including:

volume concentration of dispersed phase,
viscosity of continuous phase,
size and distribution of dispersed particles,
temperature, and
shear rate.

Since in this study rheological data has been collected at constant temperature (room temperature), temperature is not a variable. Also, preliminary experiments indicated that size and distribution of dispersed particles did not vary significantly with the dispersed phase concentration for constant speed of stirring. The viscosity of continuous phase was also constant. Therefore, there are only two variables will be considered: dispersed phase concentration and shear rate.

Richardson's equation (20) is very often used to correlate the data of emulsion viscosity (21-22):

$$\mu_r = \exp(K, \phi) \quad (23)$$

where μ_r is the relative viscosity of emulsion (which is defined as the ratio of emulsion to external phase viscosity), ϕ is the dispersed phase concentration and k_1 is a constant. However, it is necessary to point out that this equation is valid only for Newtonian emulsions and emulsions behave like Newtonian fluids only at low (usually less than 30%) dispersed phase concentrations. At higher dispersed concentrations, viscosity of emulsions will also depend on shear rate. Figure 12 shows the plot of relative viscosity (at a shear rate of 200 s^{-1}) and plastic viscosity, which is the slope of the linear portion of stress vs. shear rate curve, against dispersed phase concentration. The data plotted in Figure 12 is obtained from the Fan viscometer and is for oil-in-water emulsions. It is obvious from the figure that Richardson's equation is not valid for concentrated emulsions.

According to Richardson's equation μ_r versus ϕ should be linear on a semi-log plot. A linear relationship exists only at lower concentrations ($\phi \leq 30\%$). The viscosity of emulsions is higher at lower shear rates indicating that emulsions are shear-thinning.

Figure 13 shows a plot similar to Figure 12 but for water-in-oil emulsions. As for the oil-in-water emulsion Richardson's equation again fails to correlate higher concentration data. The relationship between relative viscosity and ϕ is linear only for ϕ less than 25%. Water-in-oil emulsions are also shear-thinning as shown by Figure 13.

EFFECT OF SHEARING IN THE RHEOGONIOMETER ON THE STRUCTURE OF THE EMULSION

In Figure 14, photomicrographs of 70% oil-in-water emulsion before and after shearing (shearing done for 5 minutes at 340.56 sec^{-1}) are presented. On comparison of the photomicrographs, it is evident that particle size and distribution was not significantly altered during rheological testing in the Rheogoniometer.

CONCLUSIONS

The main conclusions of this study are:

1. Up to 70% oil concentration, oil-in-water emulsions do not exhibit abnormal wall effects. The flow curves obtained from coaxial cylinder and cone-and-plate viscometers are essentially the same. At concentrations greater than 70%, "slip effects" are present in the Weissenberg Rheogoniometer. The Rheogoniometer gives appreciably lower viscosities than the Fan viscometer at the same shear rate (for the same emulsions) and this is probably due to the slip effects at the walls of the cone and plate viscometer.
2. Up to 60% water concentration, water-in-oil emulsions do not exhibit "slip effects." The flow curves obtained from the Fan viscometer and Weissenberg Rheogoniometer are the same. At concentrations greater than 60%, "slip effects" are present in the Weissenberg Rheogoniometer and the viscosities determined by the Rheogoniometer are much lower than those given by the Fan viscometer.

3. Flow curves obtained from Fan and Brookfield viscometers exhibit yield stress for concentrated oil-in-water and water-in-oil emulsions. However, the cone-and-plate viscometer does not exhibit yield stress. This also supports the slip effect theory.
4. Higher concentration emulsions (both oil-in-water and water-in-oil) do not follow Richardson's equation even for constant rate of shearing. Curvature in the plot of $\log \mu_r$ against $\dot{\gamma}$ is seen at higher $\dot{\gamma}$. Thus the emulsions are non-Newtonian in nature.
5. A method of estimation of continuous phase film thickness (which leads to "slip" effects) has been developed. The film thickness decreases with increased concentration of emulsion.
6. Photomicrographs of 70% oil-in-water emulsion before and after shearing in the Rheogoniometer (at 340.56 s^{-1}) revealed that particle size and distribution of emulsion was not significantly altered during testing in the Rheogoniometer.

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NOMENCLATURE

d_0	gap width between truncated cone tip and flat platen
d	thickness of the continuous phase film formed adjacent to cone and plate surface
D.R.	dial reading
k_1	instrument constant defined by Eqn. 5
k_2	instrument constant defined by Eqn. 6
K	consistency index, Eqn. 15
K^1	constant in Eqns. 12 and 13
K_2	constant in Eqn. 1
K_3	constant in Eqn. 2
ℓ_2	radius of transition from lubricated plug flow to complete laminar flow

n	flow behaviour index, Eqn. 15
y	radial distance
R	radius of cone
R_1	radius of inner cylinder (bob) of coaxial cylinder viscometer
R_2	radius of outer cylinder (rotor) of coaxial cylinder viscometer
T	torque
S	Eqn. 3

Greek Letters

α	cone angle
β	R_2/R_1 , ratio of radius of outer cylinder to inner cylinder of coaxial cylinder viscometer
ΔT	transducer reading
ϕ	volume concentration of dispersed phase
$\dot{\gamma}$	shear rate
$\bar{\gamma}$	mean shear
γ_1	maximum rate of shear without any complete laminar flow
μ	viscosity
μ_w	viscosity of continuous phase film formed adjacent to cone and plate surface
Ω	angular velocity
τ	shear stress
τ_0	yield stress
$\bar{\tau}$	mean shear stress

REFERENCES

1. Steinhauhoff, F., "Modern Oilfield Demulsification, Part 1", Petroleum, Vol. 25, Sept. 1962, 294-296.
2. Lamb, M.J. and Simpson, W.C., "Pipeline Transportation of Wax-Laden Crude Oil as Water Suspension", Sixth World Petroleum Congress, Section VII, paper 13, Frankfurt, Germany, June 1963.
3. Simon, R. and Poynter, W.G., "Pipelining Oil/Water Mixtures", U.S. Patent 3,519,006, 1970.
4. Marsden, S.S. and Raghavan, R., "A System for Producing and Transporting Crude Oil as Oil-in-Water Emulsions", Journal of the Institute of Petroleum, Nov. 1973, 59, No. 570,273,278.
5. McAuliffe, C.D., Simon, R., and Johnson, C.E., Jr., "Pumping Viscous Crude", U.S. Patent 3,467,195, Sept. 16, 1969.
6. Simon, R., et al., "Pipelining Crude Oils", U.S. Patent 3,487,844, Jan. 6, 1970.
7. Simon, R. and Poynter, W.G., "Down-Hole Emulsification for Improving Viscous Crude Production", J. of Pet. Tech., Dec. 1968, 20, No. 12, 1349-1353.
8. Alvarado, D.A. and Marsden, S.S., "Flow of Oil-in-Water Emulsions Through Tubes and Porous Media", Society of Petroleum Engineers Journal, Dec. 1979, pp. 369-377.
9. Krieger, I.M. and Maron, S.H., J. Appl. Phys. 1954, 25, 72.
10. Wilkinson, W.L., "Non-Newtonian Flow", Pergamon Press 1960, pp. 128-129, pp. 28-30 (1960).
11. Baines, W.D., "Laminar Flow of Dilute Fiber Suspensions", Report MH-73, Ottawa, National Research Council of Canada, Aug. 22, 1958.
12. Richardson, R.J., "The Flow of Wood Pulp Slurries", Sc.D. Thesis in Chemical Engineering, MIT, June 1954.
13. Kuzicki, W. and Tiu, C., Chem. Eng. Sci., 23, 231, 1968.
14. Vand, V., J. Phys. Colloid Chem. 52, 277; 300 (1948).
15. Sherman, P., "Emulsion Science", Academic Press, 1968, p. 223.

16. Furgaes, O.L. Robertson, A.A. and Mason, S.G., "Proceedings 44th Annual Meeting of Technical Section, Can. Pulp and Paper Association", pp. 79-90, Montreal, Jan. 1958.
17. Oldroyd, J.G., J. Colloid Sci., 1949, 4, 333.
18. Boardman, G. and R.L. Whitmore, "The Behaviour of Bingham Fluid in the Cone-and-Plate Viscometer", Brig. 5, Appl. Phys., 1963, Vol. 14, pp. 391-395.
19. Reiner, M., "Deformation, Stress and Flow", London: Lewis, 1960 ed., p. 278.
20. Richardson, E.G., "The Flow of Emulsions", J. of Colloid Science, (1958), pp. 367-373, Vol. 8.
21. Mao, M.L. and Marsden, S.S., "Stability of Concentrated Crude Oil-in-Water Emulsions as a Function of Shear Rate, Temperature and Oil Concentrations", J. of Can. Pet. Tech., April-June 1977, Montreal, pp. 54-59.
22. Steinborn, R. and D.L. Flock, "The Rheology of Heavy Crude Oils and Their Emulsions", J. Can. Pet. Tech., Sept. - Oct. 1983, Montreal, pp. 38-52.

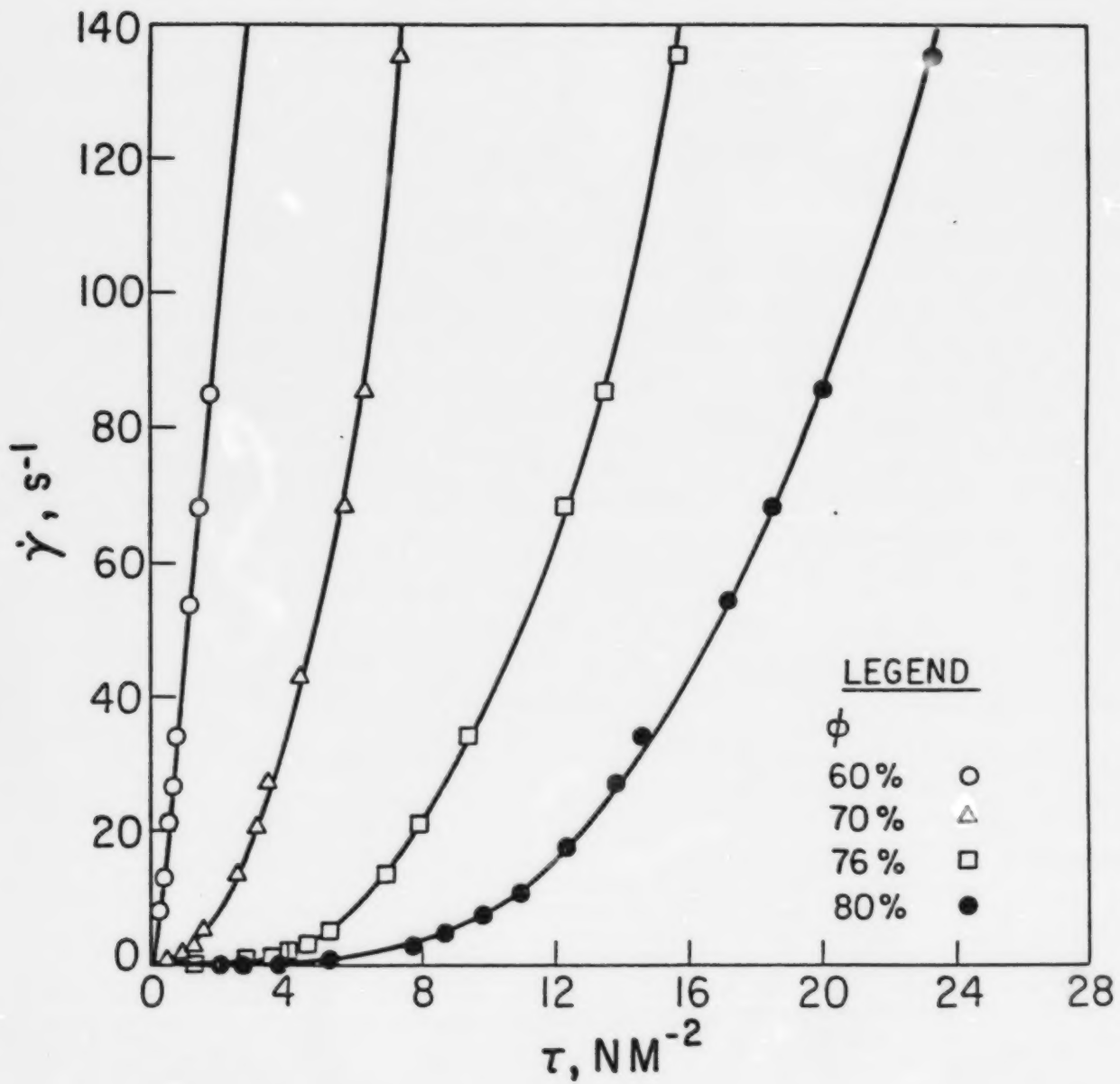


Figure 1 - Flow curves of oil-in-water emulsions obtained by a Weissenberg Rheogoniometer

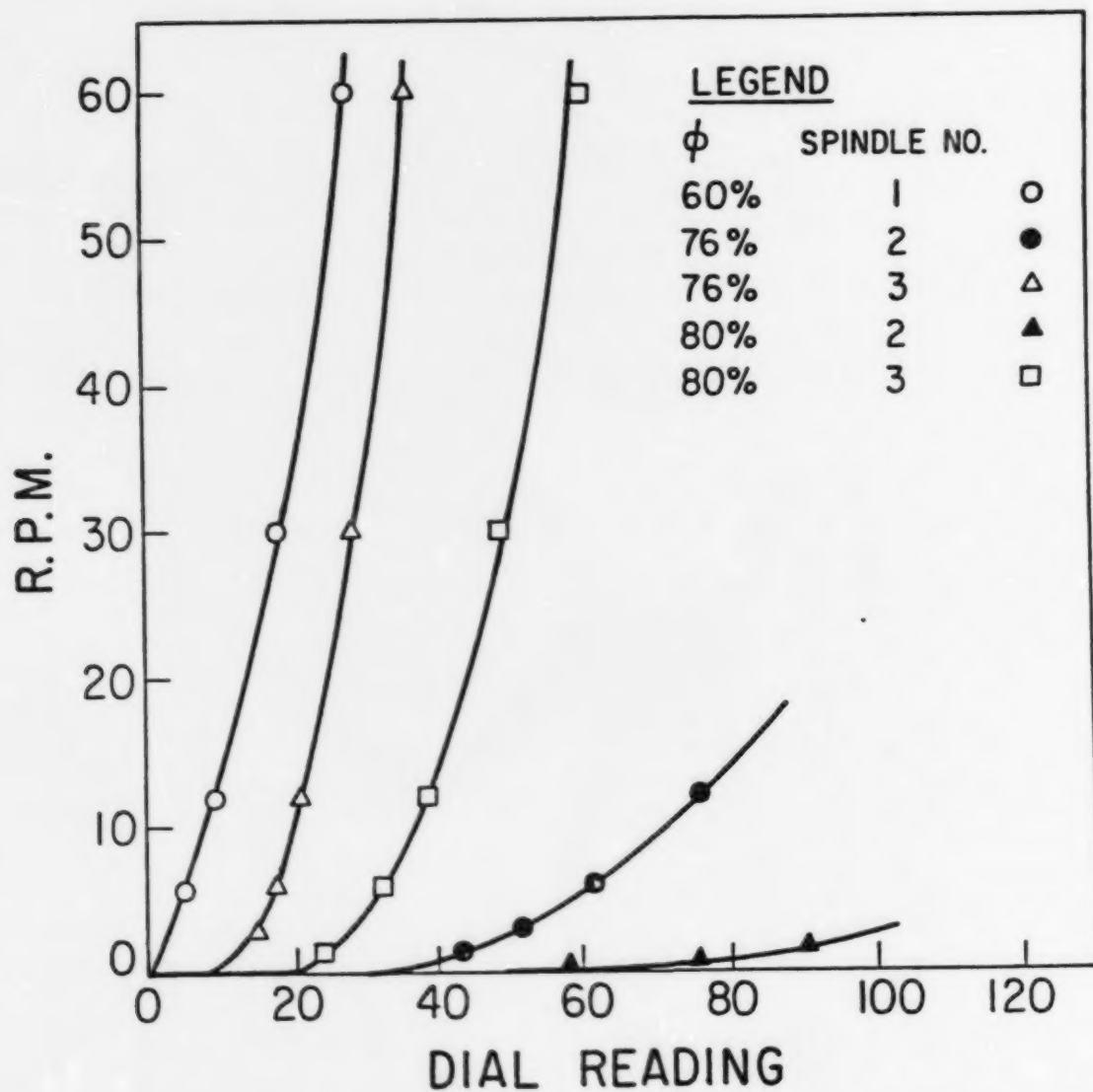


Figure 2 - Flow curves of oil-in-water emulsions obtained by the Brookfield viscometer

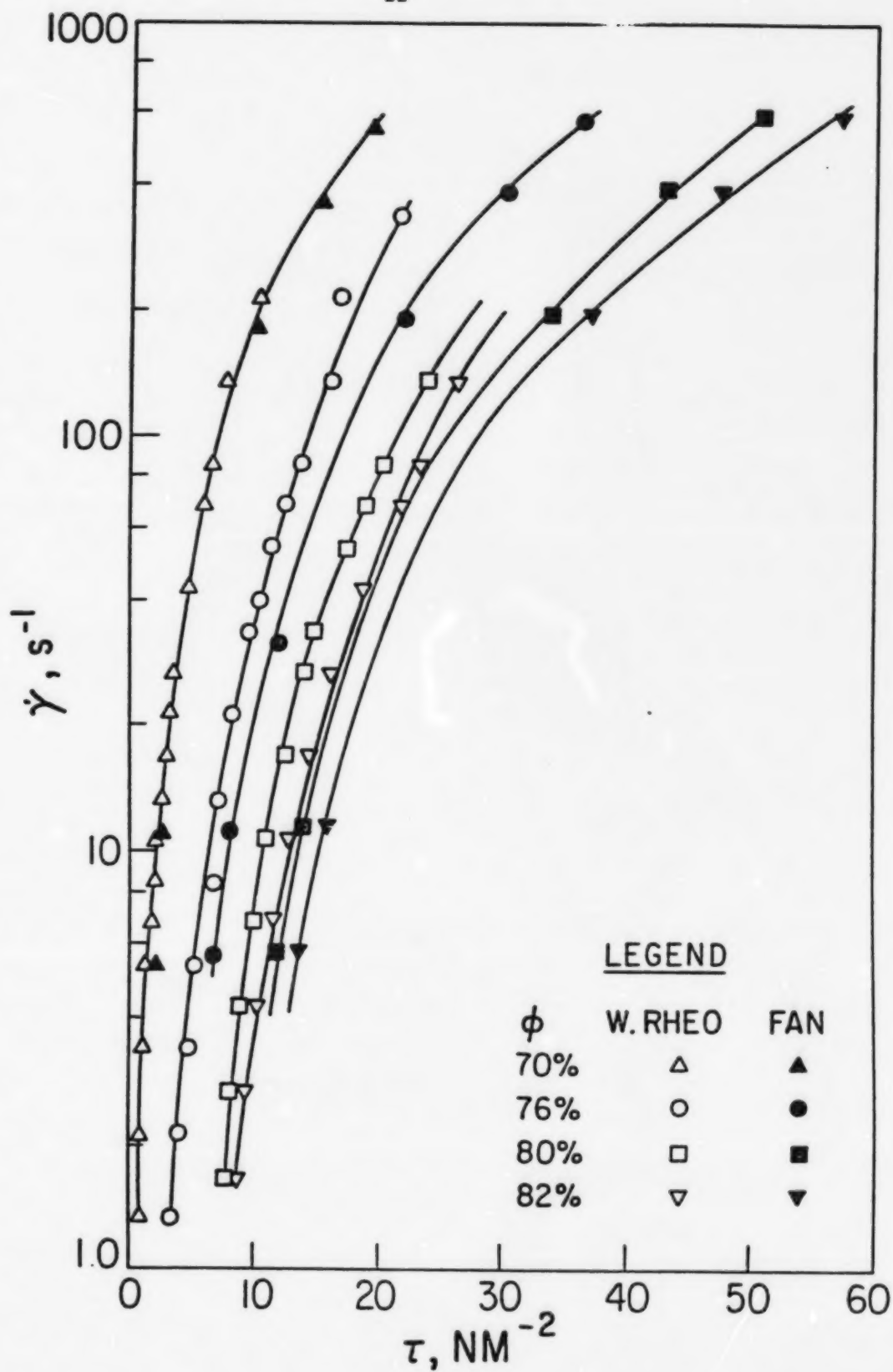


Figure 3 - Comparison of higher concentration oil-in-water emulsion data obtained from different instruments

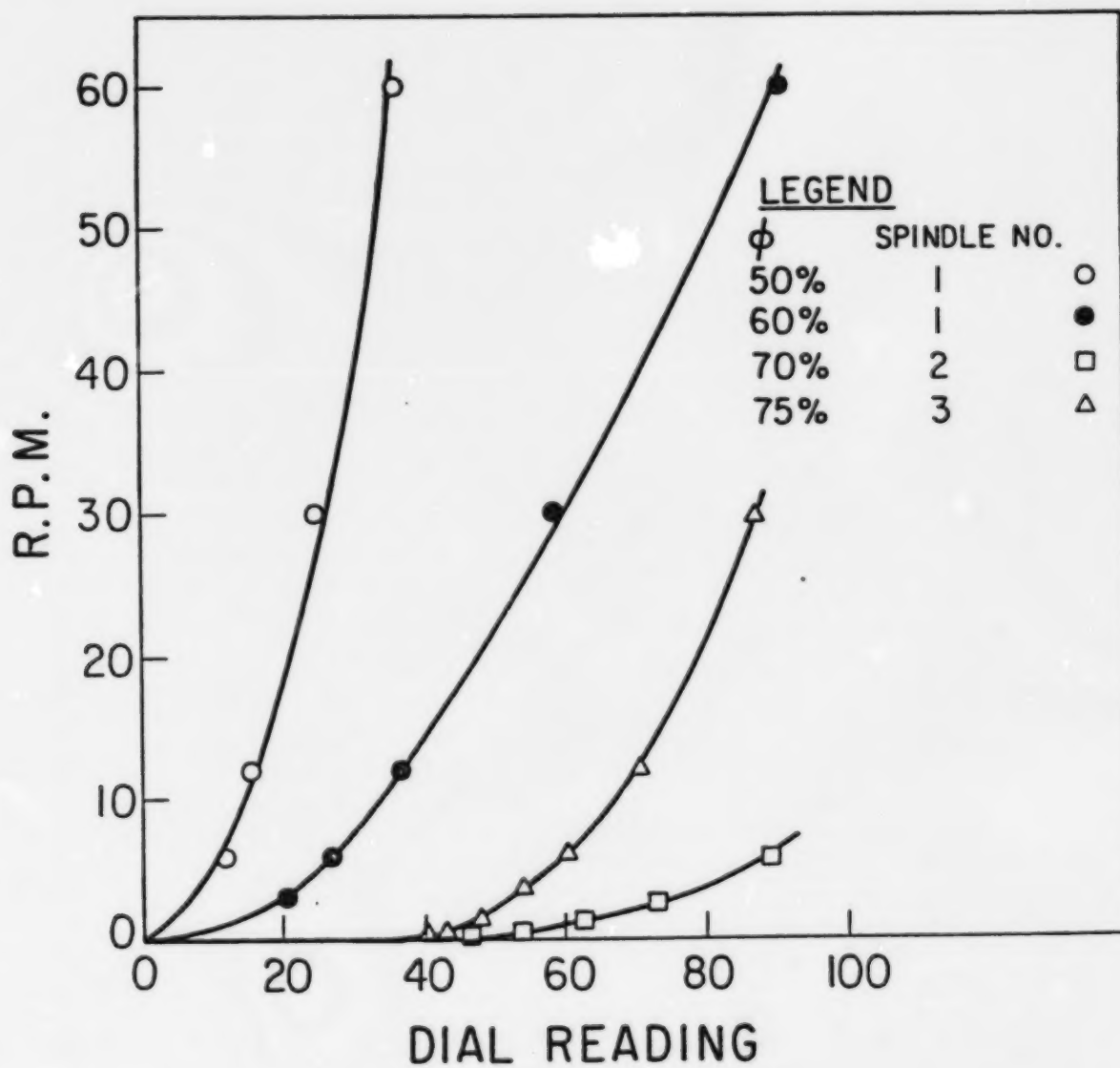


Figure 4 - Flow curves of water-in-oil emulsions obtained by a Brookfield viscometer

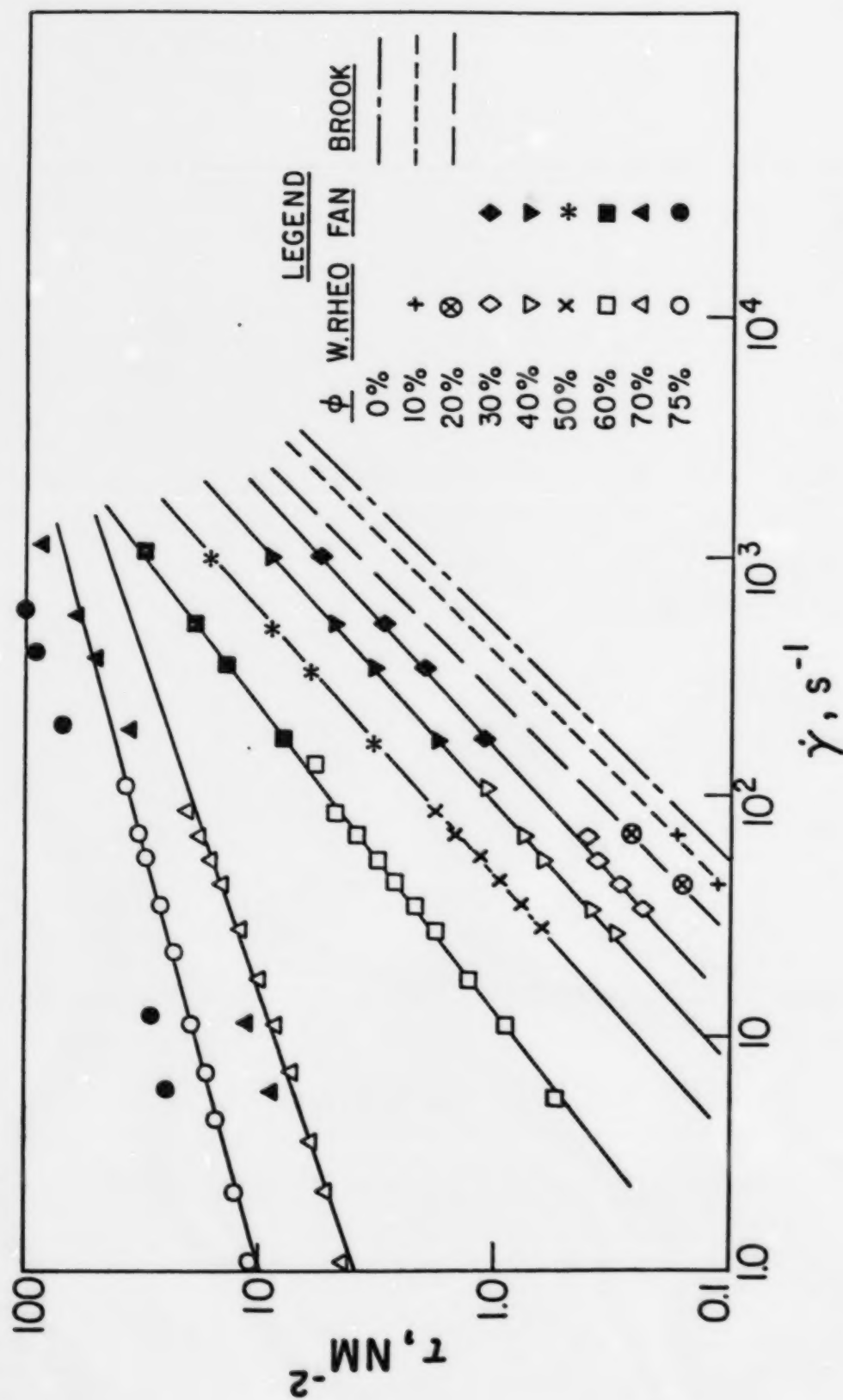


Figure 5 - Comparison of flow curves of water-in-oil emulsions obtained from different instruments

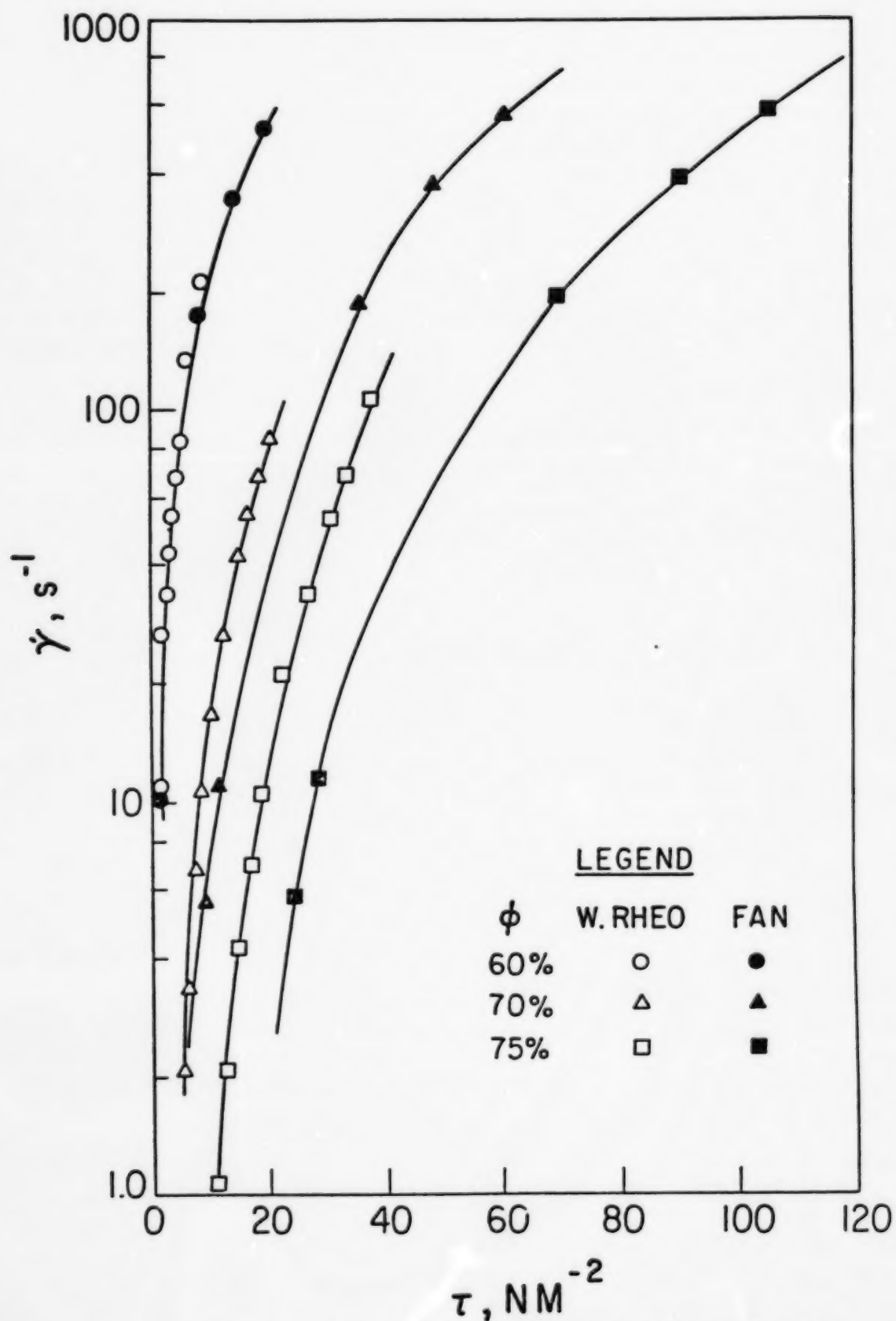


Figure 6 - Comparison of higher concentration water-in-oil emulsion data obtained from different instruments

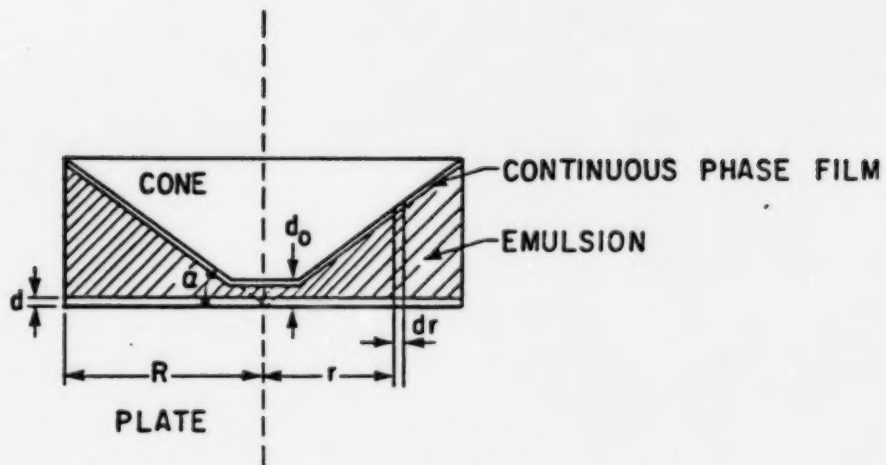


Figure 7 - Schematic of Weissenberg Rheogoniometer

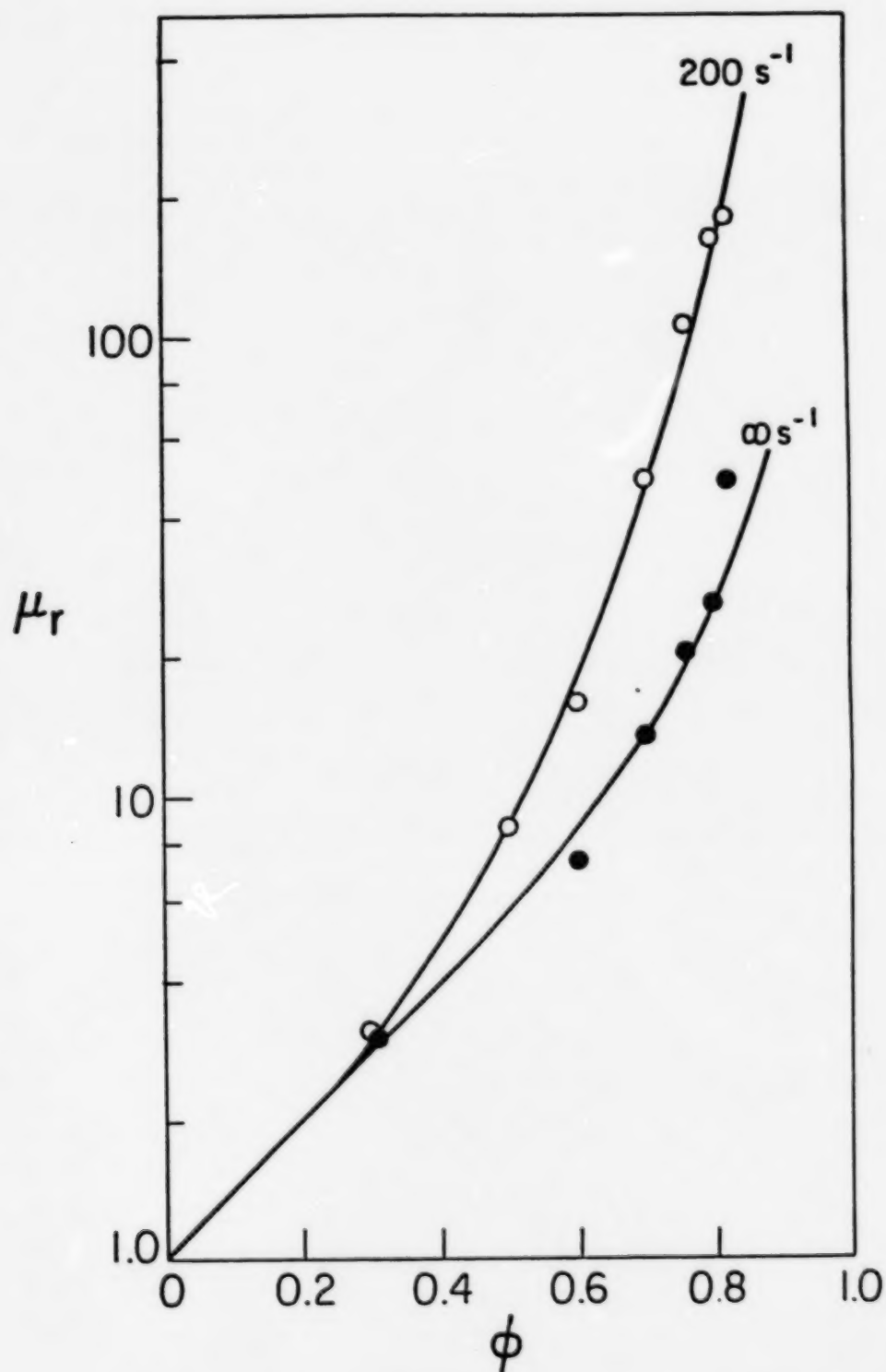


Figure 8 - Relative viscosity versus the oil concentration for oil-in-water emulsions

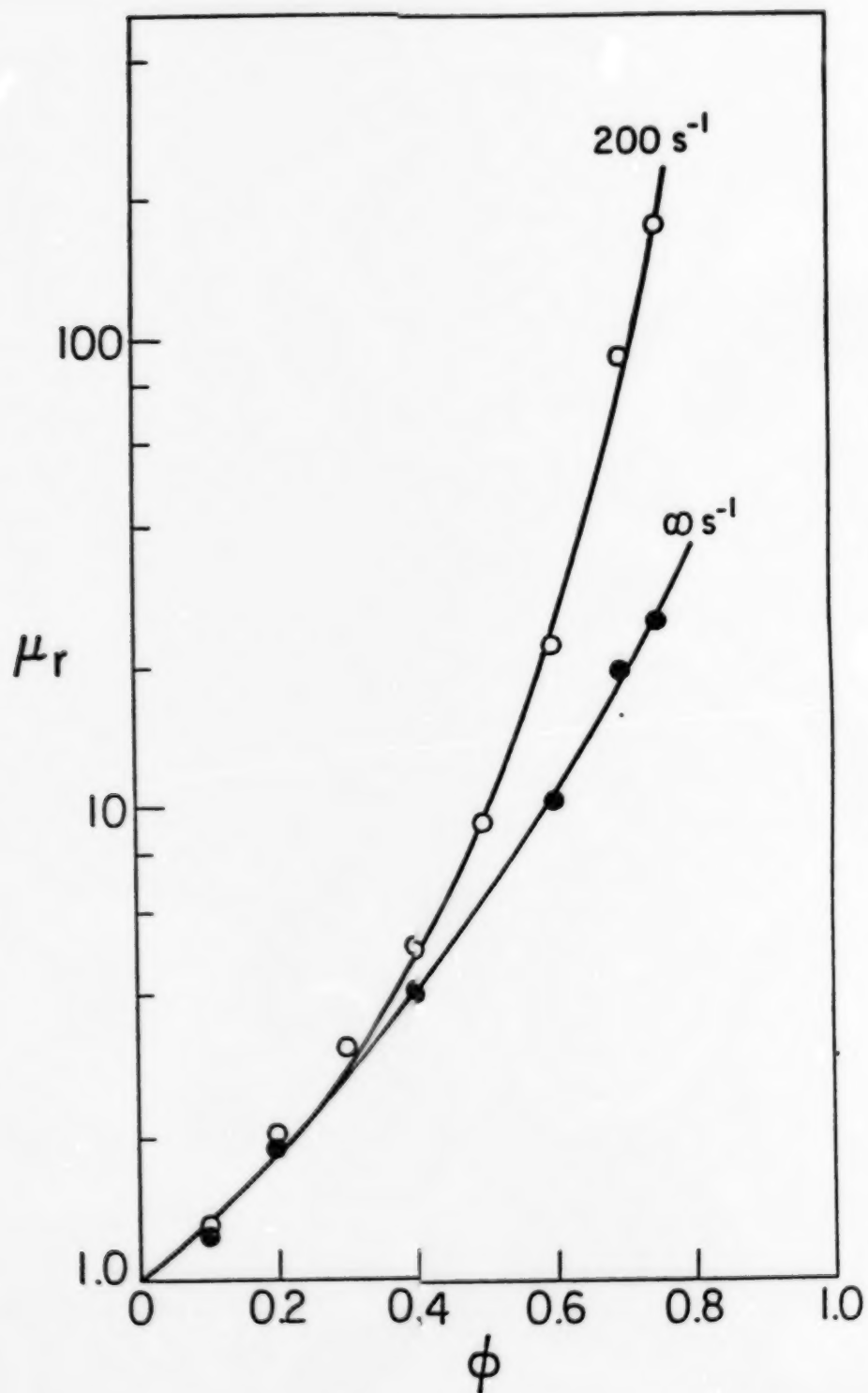
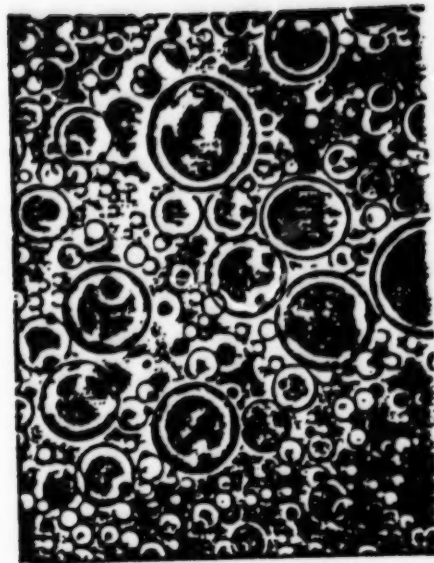
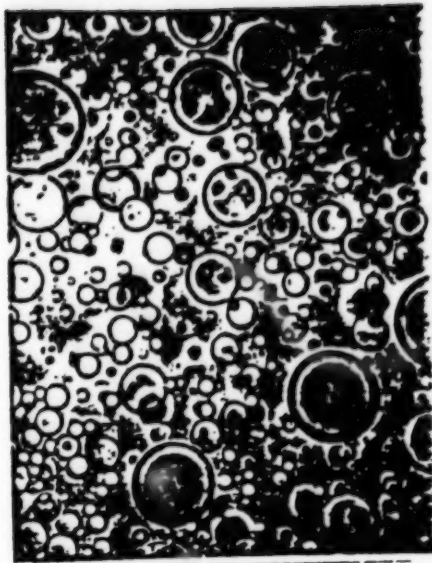
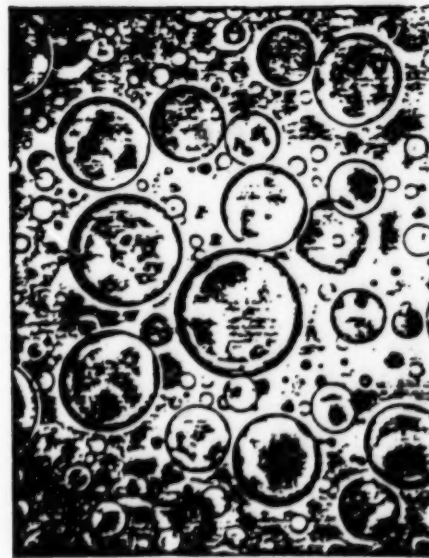
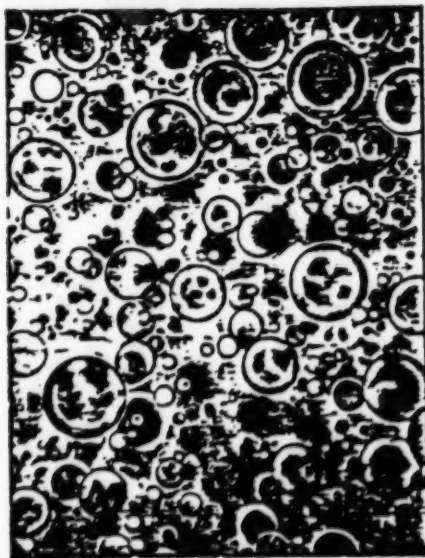


Figure 9 - Relative viscosity versus the water concentration for water-in-oil emulsions



Photomicrographs before Shearing



Photomicrographs after Shearing

Fig. 10 - Photomicrographs of 70% o/w emulsion before and after shearing